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GLASSFORMATION IN THE SYSTEM $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$

I.B.Bakhtiyarli, G.M.Fatullayeva, O.Sh.Kerimli

M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan

gulnarfatullayeva@gmail.com

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Boundaries of glassformation in the system $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ were studied using methods of physico-chemical analysis (X-ray analysis, Raman spectra, Scanning electron microscope). It was established that in glassformation region the range of concentration covers from $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ it is 13 mol%. Samples in the region of glassformation are stable at 300 K to air, water and organic solvents. Samples decompose in mineral acids and alkalis. In the region of glassformation at a temperature of 300 K were studied samples of density and microhardness.

Keywords: glassformation, As_2S_3 , stoichiometric composition, Raman spectra, diffractogram.

Introduction

Glasses prepared on the basis of arsenic sulphide are used in electrophotographic cylinders for getting flawless images and "vidicon" tubes. Photoresistors prepared on the surface of organic polymers on the basis of these glasses are very sensitive to long-wave rays. Photothermoplastic bearers are used for preparation of holographic memory and taking high-quality microfilms. Even Japan scientists Y.Onmachi, N.Uchido suggested to use these glasses for modulation of laser rays and ultra sounds [1–5]. In this connection studying the properties of obtained samples, detection of glass-formation fields in the system $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ arouse great interest.

Experimental part

In our experiments As_2S_3 and Pr_6O_{11} were used as primary components. As_2S_3 was synthesized using ampoule method from elements (As-000, sulphur – "high purity"). As_2S_3 is crys-

tallized in monoclinic syngony and crystallographic data of parameter of unit cell equals to $a=11.47$, $b=9.57$, $c=4.24$ Å; $\beta=90.27^\circ$; $Z=4$; space group $P2_1/n$ [6]. Pr_6O_{11} is crystallized in monoclinic syngony and crystallographic data equals to $a=6.6850$, $b=11.6004$, $c=12.8271$ Å; $\beta=99.97^\circ$; $Z=4$; space group $P2_1/c$ [7]. Degree of frequency of both oxides was "high purity".

In the studied system synthesis of samples consisting of primary components was weighted in accordance with stoichiometric composition, crushed into powder in agate mortar, and then quartz ampoule was placed in glassy carbon crucible. Ampoule was pumped out till the pressure of 0.133 Pa and sealed in torch flame. Synthesis was performed in stages. First quartz ampoule was kept 3 h at 875 K. Then temperature was increased up to 1050 K, synthesis was continued 4. Next tempering was conducted in an open air [8]. One of the obtained samples is shown in Figure 1.

Fig.1. $(\text{As}_2\text{S}_3)_{0.90}(\text{Pr}_6\text{O}_{11})_{0.10}$ – photo of transparent glass.

Synthesized samples were studied using the modern complex methods of physico-chemical analysis – X-ray analysis on automatic X-ray diffractometer "D2 PHASER" firm of "BRUKER", spectral analysis was carried out on spectrometer Nanofinder 30 3D Raman microscope Tokyo INSTRUMENTS, INC Japan, Density of alloys was determined using pycnometric method (filler – toluene) at 300 K. Measurement of microhardness was carried out by microhardness tester PMT-3.

Results

Boundaries of glassformation field in the system $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ were determined using the

complex methods of physico-chemical analysis. It was established that in glass formation field concentration range covers from the side of $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ 13 mol%. As to us, decrease of glass formation field Pr_6O_{11} comparing to lanthan-oxide is related to crystalline structure of oxide, i.e. the change of coordination number of lanthanides. That's why properties of lanthanide compounds are more sensitive to the change of coordination numbers relative to ionic radius. The reason of non-transparency of a glass is the formation of primary centers of crystallization in the composition, which was confirmed by the results of X-ray phase analysis and SEM (Figures 2, 3).

Fig.2. Diffractogram of alloys and primary components in the system $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$.

Fig. 3. Image of glass on Scanning Electron Microscope and chemical quantitative composition.

Color of samples in glassformation field changes from light red to dark brown. When heating glasses are dissolved in chromic mixture. They are stable at room temperature on air, in water and organic solvents. They decompose in mineral acids and alkalis. Dependence of density and microhardness on the composition of glass samples is shown in Table.

Dependence of density and microhardness on the composition in glasses, composition of $(As_2S_3)_x(Pr_6O_{11})_{100-x}$

Composition, mol	Density, g/cm ³	Microhardness, mPa
$(As_2S_3)_{0.95}(Pr_6O_{11})_{0.05}$	3.52	1450
$(As_2S_3)_{0.90}(Pr_6O_{11})_{0.10}$	3.61	1552
$(As_2S_3)_{0.85}(Pr_6O_{11})_{0.15}$	3.71	1610
$(As_2S_3)_{0.80}(Pr_6O_{11})_{0.20}$	3.82	1671
$(As_2S_3)_{0.75}(Pr_6O_{11})_{0.25}$	3.93	1737

Raman spectrum of glass of $(As_2S_3)_{0.90}(Pr_6O_{11})_{0.10}$ with excitation of long-wave laser 532 nm. It was revealed that glasses of the composition $(As_2S_3)_{0.90}(Pr_6O_{11})_{0.10}$ are

stable to the effect of laser rays. As Figure 4 shows, in spectra which characterize the bond As–S and Pr–O and intensive strengthening bands relative to primary components on waves of length 180, 226, 340 cm⁻¹ and energy slip of long waves upward leads to strengthening of covalence and, this proves hardening of the communication.

Thus, boundaries of glassformation in system As_2S_3 – Pr_6O_{11} were studied using methods of physico-chemical analysis (X-ray analysis, Raman spectra, Scanning electron microscope). It was established that in glass formation region the range of concentration covers from As_2S_3 – Pr_6O_{11} it is 13 mol%. Samples in the region of glassformation are stable at 300 K to air, water and organic solvents. They decompose in mineral acids and alkalis. In the region of glassformation at a temperature of 300 K there have been studied samples of density and microhardness.

Fig. 4. Raman spectrum of glasses of the composition $(As_2S_3)_{0.90}(Pr_6O_{11})_{0.10}$.

References

1. Vinogradova G.Z. Stecloobrazovanie i fazovye ravnovesiia v halkogenidnykh sistemakh. M.: Nauka. 1984, 176 s.
2. Ovshinsky S.R. Reversible Electrical Switching Phenomena in Disordered Structures // Phys. Rev. Lett. 1968. V. 21. No 20. P. 1450.
3. Zakery A., Elliot S.R. Optical spectroscopy of chalcogenide glasses $(\text{As}_4\text{S}_3\text{Se}_3)_{1-x}\text{Sn}_x$ // J. Non-Crystalline Solids. 2003. V. 330 (1–3). P.1–12.
4. Tsendin K.D., Bogoslovskiy N.A. Physics of Switching and Memory Effects in Chalcogenide Glassy Semiconductors // Semiconductors. 2012. V. 46. No 5. P. 559–590.
5. Venger E.F., Melnichuk A.V., Stronskii A.V. Fotostimulirovannye protsessy v halkogenidnykh stecloobraznykh poluprovodnikakh i ikh prakticheskoe primeneniye. Kiev: Akadempriodika, 2007. 283 s.
6. Lavrentev A.A., Gabrelian B.V., Nikiforov I.Ia., Vorzhev V.B. Elektronno-energeticheskaya struktura poluprovodnikovyx sulfidov As_2S_3 , AsSI , AgAsS_2 i TiS_2 // Zhurn. struktur. himii. 2005. T. 46. № 5. S. 835–842.
7. Glushkova V.B. Polimorfizm okislov redkozemelnykh elementov. L.: Nauka, 1967. 33 s.
8. Bakhtiyarly I.B., Abdullaeva A.S., Fatullaeva G.M., Kerimli O.Sh., Mirzoeva A.A. Fiziko-Himicheskie svoystva stecloobrazuyushchikh rasplavov $\text{Nd}_2\text{S}_3\text{--Ga}_2\text{S}_3\text{--EuS}$ i $\text{La}_2\text{O}_3\text{--As}_2\text{S}_3\text{--Eu}_2\text{O}_3$ // Materialy mezhdunarodnoi nauchn. konf. Tomsk: Izdatelskii Dom TGU, 2015. T. 1. 234 s.

 $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ SİSTEMİNDƏ ŞÜŞƏMƏLƏGƏLMƏ

İ.B.Bəxtiyarlı, G.M.Fətullayeva, O.Ş.Kərimli

Fiziki-kimyəvi analizin kompleks metodları (RFA, Raman spektri, SEM) ilə $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ sistemində şüşəmələgəlmə sahəsinin sərhədi müəyyən edilmişdir. Məlum olmuşdur ki, sistemin $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ tərəfində 13 mol % qatılıq intervalında şüşəmələgəlmə sahəsi müəyyənləşdirilmişdir. Alınan şüşələr mineral turşu və qələvilərin təsirindən parçalanırlar. 300 K temperaturunda havanın, suyun, üzvi həlledicilərin təsirinə qarşı davamlıdır. Şüşəmələgəlmə sahəsindəki nümunələrin 300 K temperaturda sıxlığı və mikrobərkliyi öyrənilmişdir.

Açar sözlər: şüşəmələgəlmə, As_2S_3 , stexiometrik tərkib, Raman spektr, difraktoqramm.

СТЕКЛООБРАЗОВАНИЕ В СИСТЕМЕ $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$

И.Б.Бахтиярлы, Г.М.Фатullaева, О.Ш.Керимли

Методами физико-химического анализа (РФА, Раман-спектр, СЕМ) определены границы области стеклообразования в системе $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$. Установлено, что в области стеклообразования концентрации со стороны $\text{As}_2\text{S}_3\text{--Pr}_6\text{O}_{11}$ доходят до 13 мол.%. Стекла разлагаются в минеральных кислотах и щелочах. Они устойчивы при 300 К к воздуху, воде и органическим растворителям. Изучены плотность и микротвердость образцов стекол при температуре 300 К.

Ключевые слова: стеклообразование, As_2S_3 , стехиометрический состав, Раман-спектр, дифрактограмма.